Chemical Analysis of 1794 & 1795 U. S. Silver Coins – Phase 1 Results

David Finkelstein and Christopher Pilliod – September, 2018

1.0 Overview

The single most important Mint related legislation in our nation's history was the Mint and Coinage Act of April 2, 1792. In addition to establishing the first Mint of the United States, one of the key aspects of this law was the requirement that the silver coinage was to contain 1485 parts of fine silver and 179 parts alloy (copper). This equated to 89.24278% or 89.24+% silver, and 10.75722% or 10.76-% copper.

Multiple documents stored within the National Archives and Records Administration (NARA) and the Library of Congress indicate that under the leadership of Mint Directors David Rittenhouse and Henry William de Saussure, some or all of the 1794, and most or all of the 1795 dated silver coins were produced to a 90% silver and 10% copper standard. Then, beginning in November, 1795, under the leadership of its third Director, Elias Boudinot, the Mint reverted to the 89.24+% silver and 10.76-% copper standard.

This document provides a preliminary analysis of the chemical compositions of one 1794 Cent, one 1795 Half Cent, one 1794 Half Dollar, seven 1795 Half Dollars, one 1806 Quarter, one 1807 Quarter, one 1807 Half Dollar, and one 1855-O Half Dollar. It does not include the history, overview and goals of this research project, nor does it include images and discussions of documents from the NARA and the Library of Congress related to this project. This will be done in a multi-part article series.

Note that this document uses the terms *trace* and *residual*. *Trace* refers to a relatively low amount and *residual* refers to a relatively high amount.

2.0 X-ray Fluorescence Surface Results – January, 2017

In January, 2017, Chris Pilliod performed X-ray Fluorescence (XRF) analysis on the surfaces of two circulated 1795 Half Dollars. Although the Half Dollars were approximately 2,150 microns thick, the XRF analysis could only penetrate 6 to 10 microns. Three different areas of the surface of each coin were analyzed, each identifying above standard silver content (94% - 97%), below standard copper content (2% - 4%), and silicon on the surface of each coin. See Table 1.

Note that the 1795 Half Dollars in Table 1 are listed in emission order sequence. The 1795 Overton 122 (or O-122) die marriage was struck before the 1795 O-105 die marriage.

What	Area	Silver %	Copper %	Silicon %
1795 O-122	1	97.43	2.09	0.48
	2	97.07	2.42	0.51
	3	96.36	3.11	0.53
1795 O-105	1	95.49	3.87	0.64
	2	94.45	3.92	0.63
	3	95.76	3.61	0.63

Table 1 – XRF Silver Coin Surface Analysis (January, 2017)

2.1 Copper Leaching And Environmental Contamination

Copper is much more prone to corrosion than silver. During the course of normal circulation and contact with environmental contaminants, copper will leach (dissolve) from the surface of the coins. This results in an artificially higher percentage of silver and a lower percentage of copper on the surface. Based on only the results in Table 1, It was hypothesized that the presence of silicon was a result of environmental contamination as the coins circulated.

While surface analysis employing XRF is suitable for qualitative analysis, it is an inadequate methodology to base any scientific conclusions with respect to the true composition of the coin(s) in question.

3.0 X-ray Fluorescence Subsurface Results – January, 2017

The 1795 O-122 and 1795 O-105 Half Dollars were sliced into three pieces with a diamond cutter to minimize kerf loss [the loss associated with the cutting tool]. The center piece of each Half Dollar was ground, removing approximately 10% of the metals from each side and edge, and polished to insure uniform removal. The target of 10% removal by weight was to comfortably insure that no surface effect would interfere with the results.

In January, 2017, Chris Pilliod performed XRF analysis of three different areas on the subsurface of each of the two 1795 Half Dollars. The results identified 90% - 91% silver content, 9% -10% copper content, and no silicon. See Table 2.

What	Area	Silver %	Copper %
1795 O-122	1	90.07	9.93
	2	90.38	9.62
	3	90.78	9.22
1795 O-105	1	90.04	9.96
	2	90.45	9.55
	3	91.02	8.98

Table 2 – XRF Silver Coin Subsurface Analysis (January, 2017)

3.1 Environmental Contamination Confirmed / No Trace Elements

Whereas the XRF analysis of the surface of the coins in Table 1 identified 0.48% to 0.64% silicon, no silicon was detected within the subsurface of the coins. The silicon on the surface of the coins was therefore most likely due to environmental contamination.

XRF analysis within the subsurface of the coins identified no trace elements. As a result, a better methodology was required for the level of discrimination for this project.

4.0 ICP-AES Results – February 2017

In February, 2017, Chris Pilliod sent the ground and polished center sections of the 1795 O-122 and 1795 O-105 Half Dollars to an independent laboratory. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis was performed on two different 0.5 gram samples from each coin. See Table 3.

Each sample was diluted in Nitric Acid; a highly corrosive acid. A plasma torch vaporized fine droplets of the sample at a temperature of approximately 12,000 degrees Fahrenheit. The atoms of the sample generated wavelengths that were measured by an array of semiconductor photodetectors. Note that for some elements, ICP-AES is accurate to parts per trillion.

Refer to Section 6 for analysis of the ICP-AES results.

What	Sample	Silver %	Copper %	Gold %	Lead %	Other %
1795-122	1	90.00	9.20	0.38	0.35	0.07
	2	90.02	9.18	0.38	0.35	0.07
1795-105	1	90.40	9.16	0.20	0.22	0.02
	2	90.46	9.10	0.20	0.22	0.02

Table 3 – ICP-AES Silver Coin Subsurface Analysis (February, 2017)

5.0 ICP-AES Results – Copper Coins - August, 2018

In July, 2018, Chris Pilliod sent the ground and polished center sections of one 1794 Large Cent and one 1795 Half Cent to an independent laboratory for ICP-AES analysis. The results identified 98% - 99% copper, with residual levels of lead, and trace amounts of arsenic, bismuth and silver in each coin. See Table 4.

What	Sample	Copper %	Lead %	Silver %	Gold %	Arsenic %	Bismuth %
1794 Cent	1	98.20	1.62	0.01	0.00	0.08	< 0.01
	2	98.20	1.62	0.01	0.00	0.08	< 0.01
1795 ½ Cent	1	99.00	0.36	0.08	0.00	0.37	0.15
	2	98.99	0.36	0.08	0.00	0.37	0.15

Table 4 – ICP-AES Copper Coin Subsurface Analysis (August, 2018)

5.1 There Is Arsenic, Bismuth, Lead And Silver In Copper

Arsenic, bismuth, lead and silver are generally found in copper ore. There were multiple processes available in the 18th century to remove the arsenic, bismuth and lead. These processes included liquation, roasting and smelting of the copper. Silver was separated and recovered from the copper via the parting process. All of these processes took time and cost money.

Based on entries in Mint ledgers stored at the NARA, the Mint purchased approximately 75,000 Troy pounds of copper during 1792, 1793 and 1794; including approximately 35,000 Troy pounds of copper sheets that were imported from England in 1793 and 1794. What is not known are the specific sources of the copper for any of the 1794 and 1795 copper coins, whether the copper was refined, and if any other processes were performed in an attempt to remove / part other elements. It is possible that the lead in the copper may be a combination of a trace level of it naturally being there plus a residual level from a refining process.

Whether or not parting / removal processes occurred, both coins contain a residual level of lead, and trace amounts of arsenic, bismuth, and silver. Until additional 1794 and 1795 copper coins are analyzed via ICP-AES, it is assumed that all 1794 and 1795 copper coins contain a residual level of lead, and trace amounts of arsenic, bismuth and silver.

6.0 ICP-AES Results – Silver Coins - August, 2018

In July, 2018, Chris Pilliod sent the ground and polished center sections of one 1794 O-105 Half Dollar and five 1795 Half Dollars (Overton die marriages O-117, O-115, O-116, O-109 and O-110) to an independent laboratory for ICP-AES analysis. See Table 5. The 1794 O-105 Half Dollar was donated by the Terry Brand Estate via Heritage Auctions.

Note that the 1795 Half Dollars in Table 5 are arranged by emission order sequence. Also note that Table 5 includes the results for the 1795 O-122 and 1795 O-105 Half Dollars that were analyzed via ICP-AES in February, 2017.

During 1795, the Mint struck 317,844 Half Dollars between January and June. No 1795 Half Dollars were struck after June 5, 1795. Since the seven 1795 Half Dollars in Table 5 are die marriages from the early, middle, and later parts of the 1795 emission order sequence, it can be stated with confidence that the silver for these Half Dollars was refined by the Mint over a period of several months (most likely between January, 1795 and early June, 1795).

Chris Pilliod also sent the ground and polished center sections of the subsurface of one 1806 Quarter, one 1807 Quarter, one 1807 Half Dollar, and one 1855-O Half Dollar to an independent laboratory for ICP-AES analysis. See Table 6.

What	Sample	Silver %	Copper %	Gold %	Lead %	Other %
1794 O-105	1	88.67	11.01	0.12	0.17	0.03
	2	88.75	10.81	0.12	0.17	0.03
	3	88.43	11.14	0.12	0.17	0.02
	4	88.73	10.95	0.12	0.18	0.02
1795 O-117	1	88.96	10.23	0.36	0.43	0.02
	2	88.48	10.71	0.34	0.45	0.02
1795 O-122	1	90.00	9.20	0.38	0.35	0.07
	2	90.02	9.18	0.38	0.35	0.07
1795 O-115	1	89.24	10.34	0.20	0.19	0.03
	2	89.29	10.30	0.20	0.18	0.03
1795 O-116	1	89.83	9.87	0.20	0.09	0.01
	2	89.87	9.82	0.20	0.10	0.01
1795 O-109	1	89.79	9.83	0.21	0.14	0.03
	2	90.20	9.45	0.20	0.12	0.03
1795 O-110	1	90.97	8.70	0.16	0.14	0.03
	2	91.31	8.35	0.16	0.14	0.04
1795 O-105	1	90.40	9.16	0.20	0.22	0.02
	2	90.46	9.10	0.20	0.22	0.02

Table 5 – ICP-AES Silver Coin Subsurface Analysis (August, 2018)

What	Sample	Silver %	Copper %	Gold %	Lead %	Other %
1806 Quarter	1	88.27	10.75	0.85	0.10	0.03
	2	88.35	10.69	0.82	0.10	0.04
1807 Quarter	1	88.40	10.68	0.84	0.05	0.03
	2	87.86	11.17	0.85	0.11	0.01
1807 Half Dollar	1	87.87	11.24	0.80	0.08	0.01
	2	87.78	11.24	0.83	0.11	0.04
1855-O Half Dollar	1	88.64	10.63	0.47	0.21	0.05
	2	88.95	10.22	0.48	0.28	0.07

Table 6 – ICP-AES Silver Coin Subsurface Analysis (August, 2018)

6.1 Residual Gold In The Silver

Residual levels of gold are observed in all of the silver coins dated 1794 through 1855 (see Tables 5 and 6). One valid hypothesis for this was that the furnaces, pots, and crucibles that the Mint used to refine the silver were the same used to refine the gold. As a result, the silver refining was contaminated with gold.

The rebuttal to this theory is the fact that gold is observed in the 1794 O-105 Half Dollar. The Mint's first gold bullion deposit occurred on February 12, 1795, and was made by Moses Brown. There was no gold in the Mint during calendar year 1794, therefore the residual levels of gold in the 1794 O-105 Half Dollar could not have originated from cross contamination.

Gold is generally found in silver ore. Today, gold is parted from silver via Electrolysis. Electrolysis requires electricity, which was not available in the 18th century. Parting in the 18th century was a relatively lengthy and expensive multi-step process. If, after assaying a silver bullion deposit, the Mint determined that there were significant amounts of gold in the silver, the silver deposit was withdrawn from the Mint, and not converted into coins of the United States.

6.2 Residual Lead In The Silver

Residual levels of lead are observed in the 1794 Half Dollar and the seven 1795 Half Dollars (see Table 5). During and 18th century, lead was commonly used to refine silver. The process, known as the Lead Refining Process, is summarized as follows:

1. The silver bullion is melted. Silver melts at 1,763 degrees Fahrenheit.

2. A large amount of lead is melted with the bullion. Lead melts at 621.4 degrees Fahrenheit. Lead, being more dense than silver, melts and sinks to the bottom. Lead attracts precious metals. As the lead sinks, the silver and gold adhere to it.

3. The top layer of the solution contains the non-precious metals and other trace elements (or slag layer). This slag layer is removed.

4. The remaining solution is a mixture of lead and silver, with residual levels of gold. Air is then blown over the molten mixture. Oxygen (O) combines with the lead (Pb) to form lead oxide or litharge (PbO).

5. The temperature of the furnace is raised, and the litharge is absorbed by capillary action into the furnace's hearth linings. This leaves silver, with residual amounts of gold and lead.

To date, no contemporary documents have been found that confirm that the Mint used the Lead Refining Process during 1794 and 1795. The conclusion that this process was used is based on the residual levels of lead in the silver plus analysis of Mint warrant ledgers. In order for the Mint to have refined the 366,000+ Troy ounces (or approximately 11.4 metric tons) of silver bullion deposited during 1794 and 1795 using the Lead Reining Process, large purchases of lead should have been made. Entries in Mint ledgers stored at the NARA indicate that the Mint purchased approximately 4 ½ tons of lead between December, 1792 and January, 1795. Furthermore, one entry states that the lead was specifically purchased "for refining".

6.3 Some Lead May Have Been Present In The Copper Alloy

In addition to lead being identified in the silver coins as previously described, the 1794 copper Large Cent and 1795 copper Half Cent also contain residual levels of lead. For the purpose of this analysis it is important to determine the true source of the lead found in the silver coins. Is the source of the lead the residual lead from the Lead Refining Process, a trace or residual level in the copper alloy, or a combination both? Until additional 1794 and 1795 copper coins are analyzed, it is assumed that all copper coins dated 1794 and 1795 contain residual levels of lead, and the copper used to alloy the silver also contain residual levels of lead.

For the purpose of this preliminary analysis, the assumption is being made that five eighths or 62 ½ % of the lead in the silver coins was a residual of the Lead Refining Process, and three eighths or 37 ½ % of the lead in the silver coins originated from the copper alloy.

6.4 Preliminary Conclusions Regarding Gold and Copper

What the Mint thought was refined silver was actually the amount of the silver plus the entire amount of the gold plus 0.625 times the amount of the lead.

What the Mint thought was copper alloy was actually the amount of the copper plus the entire amount of the other trace elements, plus 0.375 times the amount of the lead.

6.5 Adjusted ICP-AES Results – Silver Coins - August, 2018

Refer to Table 7 for the adjusted percentages of the silver and copper, based on the preliminary conclusions in Section 6.4.

7.0 1794: Statistical Analysis And Preliminary Conclusion

Based on the emission order sequence of 1794 Half Dollars, the 1794 O-105 was struck after the 1794 O-109 (3 known) and 1794 O-111 (1 known). It is therefore logical to conclude that the 1794 O-105 was most likely the first mass produced 1794 Half Dollar die marriage.

Chris Pilliod performed multiple T-test statistical analyses on the data for the 1794 O-105 Half Dollar in Table 7. Based on only the ICP-AES results for the 1794 O-105 Half Dollar:

1. There is a 96.9% probability that the 1794 O-105 Half Dollar was refined to a standard of 88.87% silver and 11.13% copper alloy.

2. There is a 2.8 % probability that the 1794 O-105 Half Dollar was refined to a standard of 89.24+% silver and 10.76-% copper alloy.

3. There is a 0.1 % probability that the 1794 O-105 Half Dollar was refined to a standard of 90% silver and 10% copper alloy.

Preliminary Conclusion: We are 28 times more confident that the 1794 O-105 Half Dollar was refined to a standard of 89.24+% silver / 10.76-% copper alloy as required by the Mint and Coinage Act of April 2, 1792, and not 90% silver / 10% copper alloy.

What	Sample	Silver % + Gold % + 0.625 * Lead %	Copper % + 0.375 * Lead % + Other Trace %
1794 O-105	1	88.90	11.10
	2	88.98	10.90
	3	88.66	11.22
	4	88.96	11.04
1795 O-117	1	89.59	10.41
	2	89.10	10.90
1795 O-122	1	90.60	9.40
	2	90.62	9.38
1795 O-115	1	89.56	10.44
	2	89.60	10.40
1795 O-116	1	90.09	9.91
	2	90.13	9.87
1795 O-109	1	90.09	9.91
	2	90.48	9.53
1795 O-110	1	91.22	8.78
	2	91.56	8.44
1795 O-105	1	90.74	9.26
	2	90.80	9.20

Table 7 – Adjusted ICP-AES Silver Coin Subsurface Analysis (Aug, 2018)

7.1 1795: Statistical Analysis And Preliminary Conclusion

Chris Pilliod performed multiple T-test statistical analyses on the data for the seven 1795 Half Dollars in Table 7. Based on only the ICP-AES results for the seven 1795 Half Dollars:

1. There is a 0.00 % probability that the seven 1795 Half Dollars were refined to a standard of 89.24+% silver and 10.76-% copper alloy.

2. There is a 13% probability that the seven 1795 Half Dollars were refined to a standard of 90% silver and 10% copper alloy.

3. There is a 98.8% probability that the seven 1795 Half Dollars were refined to a standard of 90.3% silver and 9.7% copper alloy.

Preliminary Conclusion: The Mint attempted to refine the metals in most, and possibly all of the 1795 silver coins to a standard of 90% silver and 10% copper alloy. This was a violation of the Mint and Coinage Act of April 2, 1792.

7.2 1794 And 1795: Preliminary Conclusions

Based on the statistical analysis results for ***both*** the 1794 Half Dollar and the seven 1795 Half Dollars, plus some historical facts, the following preliminary conclusions have been made:

1. To comply with the Mint and Coinage Act of April 2, 1792, the Mint initially attempted to refine the metals in the 1794 Half Dollars to a standard of 89.24+% silver and 10.76-% copper alloy.

2. The Dollars were the first silver coins struck by the Mint in 1794. Delivery Warrant 1 was issued on October 15, 1794 by Mint Director David Rittenhouse to transfer 1,758 Dollars from the custody of Chief Coiner Henry Voigt to the custody of Treasurer of the Mint Dr. Nicholas Way. Delivery Warrant 2 was issued on December 1, 1794 to transfer 5,300 Half Dollars from the custody of the Chief Coiner to the custody of the Treasurer of the Mint.

   Since the 1794 Half Dollars were struck after the 1794 Dollars, it is logical to conclude that the Mint also attempted to refine the metals in the 1794 Dollars to a standard of 89.24+% silver and 10.76-% copper alloy.

3. Based on the previous two preliminary conclusions, it is logical to conclude that the Mint initially attempted to refine the metals in all 1794 silver coins to a standard of 89.24+% silver and 10.76-% copper alloy.

4. Although the Mint targeted the 1794 Dollars and some or all of the remaining 1794 silver coinage to an 89.24+% silver and 10.76-% copper alloy standard, the capabilities of the Mint personnel and/or limitations of 18th century chemical and metallurgical technology prevented the Mint from achieving their targets.

5. At this time it is unclear when the Mint began refining the metals in the silver coins to a standard of 90% silver and 10% copper alloy.

Henry William De Saussure was the second Director of the Mint from July 9, 1795 through October 28, 1795. Elias Boudinot received his temporary commission as the third Director of the Mint on October 28, 1795. In a letter to President George Washington, dated December 3, 1795, Boudinot stated that immediately after taking office, he directed Mint personnel to revert to the 89.24+% silver and 10.76-% copper standard for all silver coins.

6. Between May 6, 1795 and October 24, 1795, 203,033 Dollars were transferred from the custody of the Chief Coiner to the custody of the Treasurer of the Mint. Since all of the Dollars were delivered while De Saussure was Mint Director, most or all of these coins were most likely struck to a 90% silver and 10% copper standard.

7. Between February 4, 1795 and June 5, 1795, 317,844 Half Dollars were transferred from the custody of the Chief Coiner to the custody of the Treasurer of the Mint. Since all of the Half Dollars were delivered while De Saussure was Mint Director, most or all of these coins were most likely struck to a 90% silver and 10% copper standard

8. Between March 30, 1795 and October 24, 1795, 52,516 Half Dismes were transferred from the custody of the Chief Coiner to the custody of the Treasurer of the Mint. Since these Half Dismes were delivered while De Saussure was Mint Director, most or all of these coins were most likely struck to a 90% silver and 10% copper standard.

9. On November 26, 1795, 33, 900 Half Dismes were transferred from the custody of the Chief Coiner to the custody of the Treasurer of the Mint. Since these Half Dismes were delivered while Boudinot was Mint Director, most or all of these coins were most likely struck to an 89.24+% silver and 10.76-% copper standard.

10. Regardless as to whether the Mint was attempting to refine the silver coins to an 89.24+% silver / 10.76-% copper standard, or a 90% silver / 10% copper alloy standard, the capabilities of the Mint personnel and/or limitations of 18th century chemical and metallurgical technology prevented the Mint from achieving their targets.

7.3 1795 O-117 Silver % Low And 1795 O-110 Silver % High

The ICP-AES analysis results for the seven 1795 Half Dollars are identified in Table 5. Note that the silver in the 1795 O-117 Half Dollar is lower than the other six Half Dollars. Likewise, note that the silver in the 1795 O-110 Half Dollar is higher than the other six Half Dollars. This was brought to the attention of the independent testing laboratory. They have agreed to rerun samples from the 1795 O-117 and 1795 O-110 Half Dollars at no additional cost. If the ICP-AES results change, the tables will be updated, the statistical analyses will be rerun, and the Preliminary Conclusions will be updated.